

2008 GCEP Report

Project title: Advanced Materials and Devices for Low Cost and High Performance Organic Photovoltaic Cells

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Abstract

Exciton harvesting is of fundamental importance for the efficient operation of organic photovoltaic devices. The quantum efficiencies of many organic and hybrid organic-inorganic devices are still limited by low exciton harvesting efficiencies. This problem is most apparent in planar heterostructures that suffer from a direct tradeoff between light absorption and exciton harvesting. One approach to overcome small diffusion lengths is the use of triplet excitons. We have an ongoing project investigating pentacene/C60 solar cells to determine if triplets are the dominant exciton species following photoexcitation. Simulations of exciton harvesting suggest that excitons in pentacene are triplets. These triplets are likely formed by an exciton fission route which further has implications for beating the Shockley-Queisser limit and experiments are ongoing to verify this.

In addition to using triplets to harvest excitons over long distances, we have developed a new scheme using long range resonant energy transfer to harvest singlet excitons over 25 nm away from the donor-acceptor interface in organic solar cells using resonant energy transfer. These results represent dramatic improvements over our previous findings and show that this scheme holds promise for the future design of highly efficient organic photovoltaics. We present theory and experiment demonstrating a scheme to harvest singlet excitons over 25 nm away from a donor-acceptor interface using resonant energy transfer. Improvement in materials choice could yield effective diffusion lengths as large as 40 nm using long-range transfer, while minimizing the energy loss to less than 0.1 eV making this a promising approach for developing highly efficient organic photovoltaics.

Finally, we have successfully synthesized several new low-band gap polymers. Several of these polymers have bandgap of 1.7 eV or lower. Evaluation of the performance of these new materials is underway.

Introduction

A significant fraction of the carbon released into the atmosphere is a result of burning coal and natural gas to produce electricity. It is therefore highly desirable to find ways to generate electricity without releasing carbon. The development of affordable photovoltaic (solar) cells is one of the most promising long-term solutions to keeping the CO₂ concentration in the atmosphere at safe levels.

Currently, most photovoltaic (PV) cells being manufactured are made of crystalline silicon. The average cost of the electricity that is generated in a sunny location using these cells is about two-four times more than the typical cost of electricity from the grid. Our goal is to develop technology that can reduce the cost per Watt of generation capability by at least a factor of five and hopefully even more. Our approach is to use organic semiconductors because they can be deposited onto flexible substrates in roll-to-roll coating machines, similar to those used to make photographic film and newspapers. In this project, we plan to work on three directions: (i) having significant exciton harvesting and preventing geminate recombination by using phosphorescent semiconductors, (ii) new device designs and materials required for doubling or tripling the efficiency, and (iii) new materials design concepts to improve the absorption of low energy photons by using new low band gap semiconductors that have sufficient charge carrier mobilities for charge extraction.

Results

1. Pentacene Solar Cells Incorporating Triplet Excitons

Triplet generating materials are attractive for use in solar cells because triplet excitons have long lifetimes and generally have large diffusion lengths. Most of these materials form triplets through intersystem crossing (ISC) from a singlet state through interactions with a heavy metal atom such as platinum or iridium. In pentacene, however, it has been demonstrated that triplets form through an ultrafast fission process where a singlet exciton splits into a pair of triplets.[1, 2] If this process causes the majority of photoexcited singlets to become triplets, this would explain pentacene's low fluorescence, large reported exciton diffusion length, and the high current obtained from pentacene based solar cells.[3]

In order to understand the exciton dynamics most relevant to photovoltaic performance, we performed direct, time-resolved measurements of the photocurrent generated by short (5ns) pulses of light. If the photocurrent comes from triplet excitons and if the active layer is thicker than the exciton diffusion length, then current should be generated for a time equal to the exciton lifetime as this is the maximum time over which excitons can diffuse to the heterojunction and generate current. We performed this experiment on both pentacene:C₆₀ and PtOEP:C₆₀ cells and in both cases, found that the current transient lasted for <100ns. This is a surprising result, especially for the PtOEP control devices, as this material is known to form triplets via ISC and has a confirmed triplet lifetime of 36μs when measured in a dilute guest:host matrix.[4]

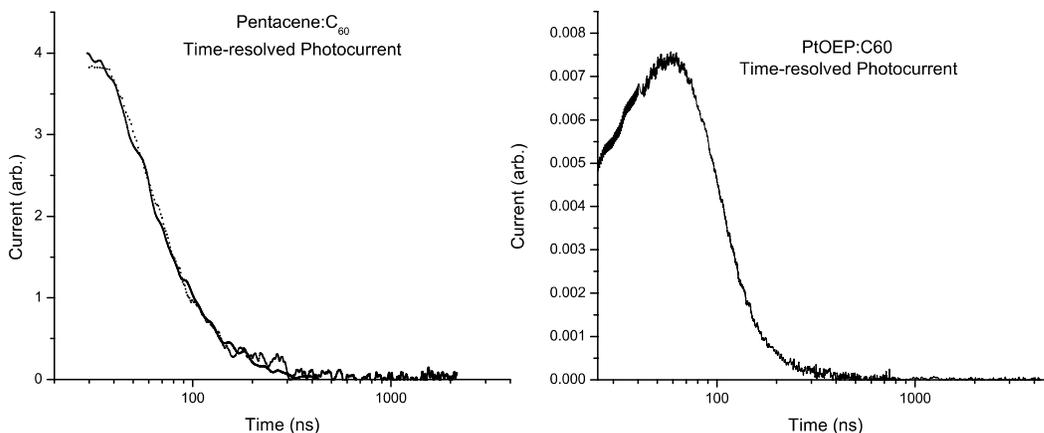


Figure 1. Time-resolved photocurrent data from PtOEP:C60 triplet control devices and from pentacene:C60 devices.

We can think of two scenarios that explain these data. One possibility is that triplet excitons have a much shorter lifetime in a film than in a dilute matrix. This possibility is not considered most of the time because phosphorescent materials are primarily used in OLEDs where they are dispersed in a guest:host configuration. Another is that the diffusion length of triplets is actually much larger than what has been published. If the diffusion length is much larger than the thickness of our active layers (~30nm), then it is possible that all of the excitons are quenched before they have a chance to decay naturally. The triplet diffusion lengths quoted in the literature for these materials are all in the range of 30-60 nm. Most of these diffusion lengths are calculated by fitting external quantum efficiency data to a model which makes numerous assumptions about the system that may be incorrect. Baldo et al. made a direct measurement of the triplet diffusion length in Alq₃ using phosphorescence emission from a dopant and found that the triplet diffusion length was greater than the bounds of their measurement capabilities (>140nm).[5]

Both of these possibilities are intriguing. If the triplet lifetime is shorter when the phosphorescent molecules are not diluted, we may need to better engineer these materials so that their interactions in a film preserve their excitons' long lifetimes. If the triplet diffusion length is longer than most believe, then it may be possible to collect excitons from much further away than we had originally thought possible. Of course, we have already experimentally optimized the thickness of the active layer; simply thickening the active layer does not solve the problem since this leads to charge collection issues due to the built-in electric field being weakened and charge carriers having to travel farther.

Before choosing to investigate either of these possibilities, we think it prudent to verify our hypotheses of the cause of the short photocurrent response. We have set up an experiment that can measure optical absorption transients and are in the process of taking data on neat films of PtOEP and pentacene at various temperatures. We will determine the exciton lifetime of these materials in the non-dilute film configuration. The variation in temperature will quantify the nonradiative decay rate. Once we have a clear picture of

what is shortening the exciton lifetimes, we will be able to optimize the devices to take advantage of the unique properties of triplets.

2. Low Bandgap Materials and Solar Cells

For polymer semiconductors, we need solution processable materials with low energy gaps, sufficient exciton diffusion lengths, high absorption and high charge carrier mobilities. Previous reported work typically only addressed some of the above problems in materials design. The great challenge is to design materials that can meet *all* of the above requirements. We think fused aromatic molecules incorporated into conjugated polymers are uniquely suited to meet all the requirements. In the past year, we have developed key enabling chemistry for the synthesis of these new classes of polymers. While continuing synthetic approach development, we started synthesizing new polymers and their evaluation for OPVs. As discussed below, we are now able to combine several desirable features in a single polymer, such as low bandgap and high charge carrier mobility. We have achieved reasonably good device performance from initial device characterization. These characterizations also revealed that the absorption coefficients and energy levels for these polymers still need to be improved. These feedbacks are being incorporated into our future material design.

2.1. Synthetic approach development

We have developed the chemistry for incorporating pentacene derivatives into conjugated polymers for the first time.[6] To demonstrate feasibility, we successfully synthesized anthradithiophene- and pentacene-containing regiorandom **polymers 1** and **2** as shown in **Figure 2**.[7] Even though these polymers are the first of their type and not yet optimized, they still show reasonable solar cell performance. **Polymer 1** was blended with the electron acceptor PCBM-C60 to make bulk heterojunction solar cells with PEDOT and aluminum electrodes. The power conversion efficiency was 0.76%, the open-circuit voltage was 0.50 V, the short-circuit current was 4.03 mA/cm², and the fill-factor was 0.38. Careful characterization of the materials and solar cells revealed several problems and motivated us to develop new chemistry to solve these problems.

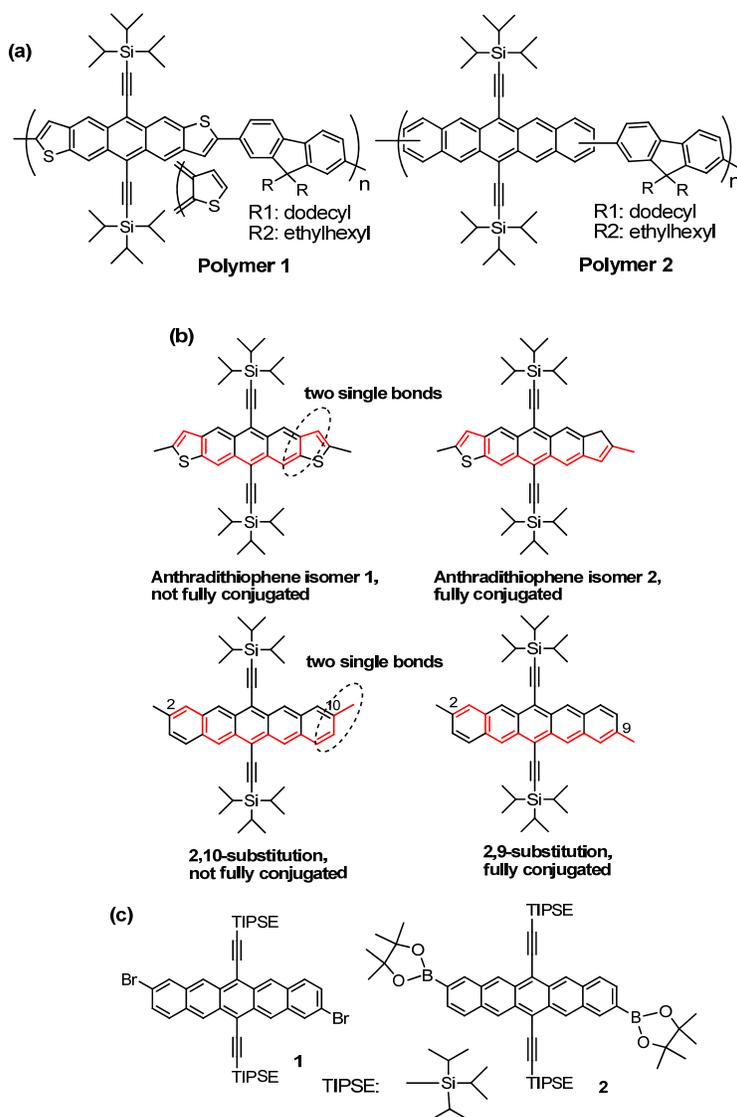


Figure 2. Schematic structures of new pentacene-containing conjugated polymers, which combines high charge carrier mobility and low bandgap.

First, the band gap was not reduced as much as we hoped. The TIPSE-anthradithiophene (TIPSE: triisopropyl silyl ethynyl) monomer has an energy gap of 2.10 eV and the corresponding polymer has a band gap of 1.91 eV. We think that the band gap could be reduced more significantly if we reduce the steric hindrance between side chains on the monomers, which resulted in a high twist angle between the monomers and reduced the wavefunction overlap between them.

The second problem is that the anthradithiophene has two isomers as shown in **Figure 2b**. One of the isomers is not fully conjugated with the fluorene comonomer, which again reduced the wavefunction overlap between them. Similarly, the pentacene-containing **polymer 2** also had two isomers with 2,9 and 2,10 substitutions (positions marked in **Figure 2b**). The 2,10-substitution does not give a fully conjugated polymer.

This promoted us to develop new chemistry for the synthesis of new 2,9-substituted **monomers 1** and **2**. They will allow us to make more fully conjugated pentacene-containing polymers.

To verify that the conjugation can be extended, we synthesized regioregular **polymer 3** using monomer **1** to compare with the corresponding regiorandom **polymer 4** synthesized from monomer **3**. Noticeably, the solution spectrum of the regioregular polymer **3** is 10 nm red-shifted compared to that of the regiorandom **polymer 4**, indicating an improved conjugation from the 2,9-substitution while the regiorandom polymer contained less conjugated 2,10-substitution. Moreover, the spectrum for thin film is significantly red-shifted by 50 nm compared to the corresponding solution spectrum, indicating strong π - π stacking between polymers and improved electron delocalization. As a comparison, the well-known high charge carrier mobility regioregular poly(3-hexylthiophene) has a red-shift of 60-80 nm from solution to thin film.[8] This result also indicates that the large bulky TIPSE groups do not suppress π - π stacking in the new polymer, which is an important requirement for good charge transport and likely the exciton diffusion.

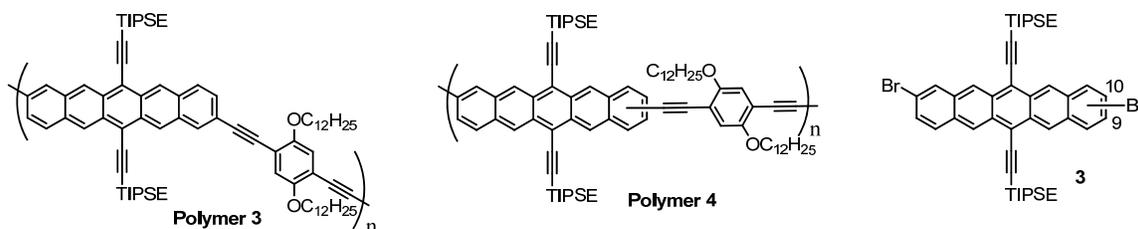


Figure 3. Regioregular polymer 3 and regiorandom polymer 4. Monomer 3 contains a mixture of 2,9- and 2,10-dibromo compounds.

The third problem was that the polymer only had a peak absorption cross section of $1 \times 10^5 \text{ cm}^{-1}$, which is about half that of the polymers commonly used in bulk heterojunction solar cells such as P3HT. We also attribute this problem to the twist between monomers. Since absorption at the band edge involves exciting an electron from a HOMO wavefunction that has its peak density in the donor monomer (the fused aromatic) to a LUMO wavefunction that has its peak density in the less electron-rich monomer (the fluorene), it is important to have the monomers in the same plane. This will be incorporated into our current new polymer design.

2.2. Efficient bandgap tuning while maintaining high charge carrier mobility.

Two general strategies can be used to reduce bandgaps of conjugated polymers. One approach is to extend the conjugation of the polymer by using large monomers (e.g. pentacene) and making the adjacent monomer units more coplanar, both of which enable the wavefunction to spread out and further reduce the bandgap. Fused aromatic molecules, such as pentacene derivatives, are attractive as monomer units because they already have relatively low energy gaps (some as low as 1.7 eV in thin films as compared to above 3

eV for other commonly used aromatic units). Incorporating them into a planar conjugated polymer will further reduce the bandgap. The steric hinderance between the H atoms on adjacent aromatic rings is the major cause for nonplanarity, therefore, inserting more thiophene-thiophene, thiophene-thioazole, thioazole-thioazole and thioazole-phenyl linkages are the most desirable followed by thiophene-phenyl linkages. Phenyl-phenyl linkages should be avoided. In addition to coplanarity, one also has to ensure that the conjugated units are substituted in positions that allow the conjugation to be fully extended through the entire polymer backbone. For example, one of the isomers of anthradithiophene and 2,10-dibromopentacene do not give fully conjugated polymers, i.e. the alternation of double and single bonds does not extend in the entire polymer. In some locations, two single bonds are connected to each other disrupting conjugation along the polymer backbone (**Figure 2b**).

The second strategy to reduce the bandgap is to incorporate electron-deficient units to make donor-acceptor type conjugated polymers.[9] Qualitatively, the electron-rich donor units push up the HOMO level of the polymer while the electron-deficient acceptor units push down the LUMO level, resulting in a lower bandgap compared to either the polymer containing just the donor or just the acceptor units.

We designed and synthesized new thienopyrazine derivatives (shown in **Figure 4**) as the acceptors. Thienopyrazine has been used as an acceptor unit in low bandgap polymers. In our work, we have extended the conjugation of the phenyl ring to naphthalene, biphenyl, bipyridine and bithiophene so that the resulting molecule is even more electron-deficient. The additional rationale for using these fused ring systems is that we expect their larger extended p-system will promote more efficient electron delocalization. We found that the bandgap of the resulting polymer was lowered from 1.8 eV for **polymer 5** with acceptor **4** to 1.65 eV for **polymer 5** with acceptor **5**. Biphenyl substitution (**polymer 5** with acceptor **6**) further decreased the band gap to 1.4 eV. Using thiophenes as comonomers, we achieved bandgap as low as 1.1 eV for **polymer 6**, which is remarkably low for organic polymers.

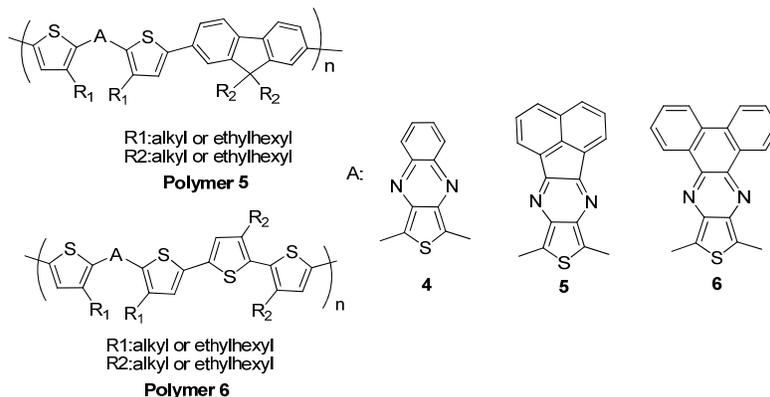


Figure 4. Thienopyrazine polymers with low bandgap and high charge carrier mobilities.

Importantly, the transistor charge carrier mobility for the naphthalene substituted thienopyrazine **polymer 5** with **acceptor 5** is as high as 0.1 cm²/Vs, which is amongst

the highest ever seen in polymers. In **polymer 5**, fluorene was chosen as a comonomer unit because it is readily available for demonstration of concept and it has been incorporated in other high performance low bandgap polymers. In our case, preliminary evaluation of bulk heterojunction solar cells was performed with PEDOT and LiF/aluminum electrodes for **polymer 5** with **acceptor 5** blended with the electron acceptor PCBM-C60. The power conversion efficiency was 1.38%, the open-circuit voltage was 0.52 V, the short-circuit current was 5.35 mA/cm², and the fill-factor was 0.50. We will significantly improve the performance of this class of polymers by incorporating more coplanar monomers and optimizing the position of the sidechains.

Our results with **polymer 5** indicate that extended conjugation in the acceptor unit in conjunction with more planar monomer-monomer linkages indeed can significantly lower bandgap of the resulting polymer. The mobility of **polymer 5** with **acceptor 6**, however, is lower compared to with **acceptor 5**. The charge transport in conjugated polymer film is through both intrachain transport and interchain hopping. Having a planar fully conjugated backbone allows better intrachain charge transport. For efficient interchain charge transport, good π - π overlap between polymer backbones is essential. To promote long range π - π stacking, it has been shown that sidechain substitution should be designed to allow good sidechain interdigitation.[10] It is likely that the slightly larger biphenyl unit reduced the space available for sidechain interdigitation. We will solve this problem by adding one additional thiophene unit in between the acceptor and rest of the comonomer units.

Another problem we observed with the ultra low bandgap **polymer 5** with **acceptor 6** is that the PV cell open circuit voltage is quite low. This is likely a major reason for lower efficiency compared with using **acceptor 5**. We need to pull down the HOMO level of this polymer to increase Voc. This could potentially be accomplished by replacing the thiophene units with thioazoles, which is underway.

Future Work

The above studies indicated that our current material designs are promising for achieving low bandgap and high charge carrier mobilities. We understand the remaining problems to address in order to achieve high power efficiency with our new polymers. We will incorporate necessary structural design and modifications into these polymers and we expect that significant improvement in solar cell efficiency will be realized.

2.3 Development of New Assays to Understand loss mechanisms in OPVs

In parallel to the analyses of the devices and materials mentioned above, McGehee has been developing a battery of tests to diagnose loss mechanisms in organic photovoltaics. Development of better materials requires feedback for prototypes which suggests directions for improvement. We have used a variety of device tests and structural characterization techniques to investigate loss mechanisms in organic cells and plan to apply these techniques to diagnose the new material systems made by Bao.

P3HT:PCBM Blends

To demonstrate this approach, McGehee has done a thorough systematic device study of the most efficient single-junction polymer-based OPV system, P3HT:PCBM.

Efficiencies for the P3HT:PCBM blend architecture of ~4.5% have been reported as well as a parallel full structural characterization. Using the approach discussed below, we have determined geminate recombination to be primarily responsible for limiting the efficiency in this material system.

A major question for any PV system is:

- What limits the efficiency?

This can be further broken down to:

- What limits the J_{sc} ?
- What limits the FF?
- What limits the V_{oc} ?

The FF is most often limited by a charge carrier mobility that is too low, which increases space charge effects and/or recombination. The V_{oc} of many organic PV systems is simply limited by overly large band offsets. The question of J_{sc} is much more complicated. McGehee has developed tools to address this complexity.

The primary parameter that determines the J_{sc} is the external quantum efficiency, η_{EQE} , which is the number of electrons collected per photons incident on the cell. The EQE can be separated into the individual processes from light absorption to charge extraction as shown in the following equation.

$$\eta_{EQE}(\lambda, V, I) = \eta_A(\lambda) \cdot \eta_{ED} \cdot \eta_{CT} \cdot \eta_{CC}(V, I)$$

For emphasis it is shown the EQE is wavelength (λ), voltage (V), and light intensity (I) dependent. The absorption efficiency (η_A) gives rise to the wavelength dependence in the EQE due to the absorption spectrum of the active layer whereas the charge collection efficiency (η_{CC}) gives rise to both the voltage and intensity dependence in the EQE. The exciton harvesting efficiency (η_{ED}) and charge transfer (exciton dissociation) (η_{CT}) efficiencies are, to first order, both independent of wavelength, voltage, and intensity and only depend on the materials employed and the domain sizes of the nanostructures formed.

For the P3HT:PCBM system we have systematically investigated each of these processes through modeling and experiment and determined the primary loss is in η_{CC} , due to geminate recombination, and an additional loss is in η_A due to parasitic absorption and reflection losses.

Light Absorption

We have developed a thin film model that considers the coherent reflection and transmission of light at each planar interface in the device. We use measured optical properties of each material in the device to determine where the light is absorbed and where it is reflected.

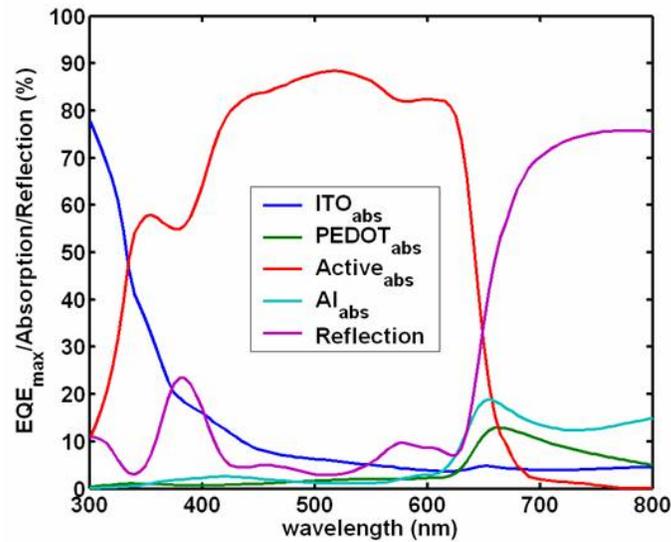


Figure 5: Reflection and absorption in various layers of a P3HT:PCBM solar cell.

Figure 5 shows this as a function of l for a 1:1 P3HT:PCBM blend. The red curve is the predicted η_A , which peaks at nearly 90% near 500 nm. This is theoretically the maximum achievable EQE in the P3HT:PCBM system. Also shown is the parasitic absorption in the transparent conductor (ITO) (blue curve), PEDOT (green curve), and aluminum (Al) (light blue curve) as well as the total specular reflection loss (purple curve).

Integrating the above η_A spectrum with AM1.5G solar spectrum gives $\sim 14 \text{ mA/cm}^2$. This is what the J_{sc} could be if all other processes (exciton harvesting, exciton dissociation and charge collection) were perfectly efficient. State-of-the-art cells typically give only $\sim 10 \text{ mA/cm}^2$.

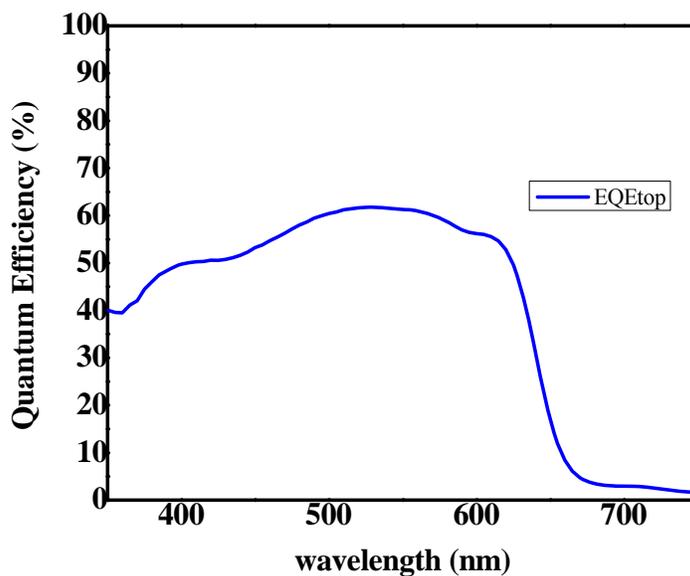


Figure 6: External quantum efficiency of a 200-nm-thick P3HT:PCBM cell.

Figure 6 shows a typical experimental EQE curve measured for a 200 nm P3HT:PCBM cell made in McGehee's lab.

The shape of the experimental curve and theoretical curve is qualitatively similar but the peak quantum efficiency is typically only 60-65% rather than ~90% as theoretically predicted. Thus ~1/3 of the photons absorbed in the active layer do not result in collected charge.

Exciton Harvesting and Charge Transfer

We and others have performed luminescence quenching studies and have shown that nearly 100% of the P3HT luminescence is quenched, which indicates near perfect exciton harvesting and dissociation (i.e. $\eta_{ED} \cdot \eta_{CT} \sim 100\%$). Exciton quenching is highly effective because the polymer domains are quite small.

Charge Collection

The above evidence necessarily implies that the EQE of this system is limited by charge collection. Charge collection can be imperfect due to geminate recombination (the recombination of the charge pair initially formed following exciton dissociation) or bimolecular recombination (recombination of a charge created from one exciton with the opposite charge of another exciton during transport to the electrodes). Both of these recombination pathways can be enhanced by the build-up of charge, due to imbalanced carrier transport, which can redistribute the electric field in the device suppressing charge extraction. By controlling the light intensity, the relative role of geminate and bimolecular recombination and space charge can be distinguished since bimolecular recombination and space charge are strongly dependent on the density of carriers in the device but geminate recombination is not.

1:1 p3ht:pcbm

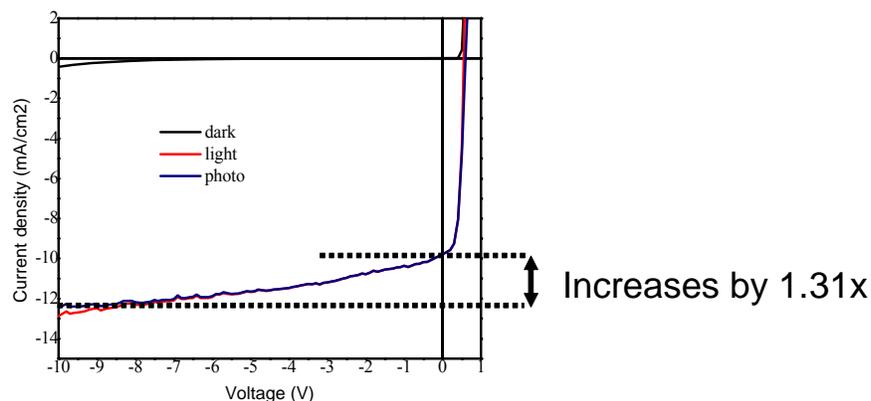


Figure 7: Current-Voltage curve of a 200-nm-thick P3HT:PCBM cell.

Figure 7 shows current-voltage characteristics for the same solar cell the EQE was measured for. We see that there is a significant increase in the photocurrent when applying a large reverse bias ($\sim 10\text{V}$) beyond which the photocurrent saturates. The increase in photocurrent is approximately equal to the ratio of theoretical to experimental peak EQE. This shows that by applying a large reverse bias the charge collection efficiency can be made near perfect. We have controlled the light intensity and found that the increase from 0 V (at J_{sc}) to saturation at high reverse biases is not dependent on light intensity. This allowed us to rule out both bimolecular recombination and space charge as responsible for the imperfect collection at short circuit. Thus geminate recombination in this system is the primary loss mechanism in the photocurrent.

Conclusions

We have systematically investigated the loss mechanisms in the leading OPV system, P3HT:PCBM and determined that a primary loss in photocurrent is due to imperfect charge collection due to imperfect geminate separation. Approximately 25% of the geminate pairs are not split under short circuit conditions. If this loss mechanism was eliminated and light absorption in the ITO were eliminated, as our optical modelling showed, cell efficiencies over 6% are within reach. Further, this systematic study was used to develop the battery of tests which will be similarly applied to new materials systems generated by Bao.

pBTTT:PCBM Blends

(3-alkylthiophen-2-yl) thieno[3,2-*b*]thiophene) (pBTTT) (inset to figure 8) has been chosen as a model polymer with which to further develop the battery of tests. pBTTT has recently demonstrated a high mobility when measured in a field effect transistor as a consequence of large scale crystallization, but has never been demonstrated in a solar cell. This high crystallinity makes this system easy to study with a variety of analytical techniques. As a first step, pBTTT:PC₇₁BM solar cells were fabricated with a varying amount of fullerene and a max efficiency of $\sim 2.4\%$ was achieved (figure 8).

Surprisingly the device was optimized with the addition of 80% fullerene. A blend incorporating 50% fullerene produced almost zero current even though all excitons were harvested as evidenced by complete photoluminescence quenching. All amorphous polymer:PCBM systems studied in the literature (including the low-bandgap polymers mentioned above) demonstrate an optimal blending ratio around 1:4, whereas a 1:1 ratio is ideal for semicrystalline polymers like P3HT. To date, there has been no overlying theory as to why this ratio is ideal. For some polymers, this has been attributed to a 100-fold increase in the mobility with blending as well as improved phase separation. The mobility in the pBTTT phase at all blending ratios is high enough to eliminate the effects of space-charge. It would then seem that the phase separation and crystallinity change with blending ratio until an ideal structure is reached in a 1:4 blend. As will be shown, the McGehee group has determined that the chemical structure of the pBTTT allows for intercalation of PCBM such that a large amount of PCBM is needed in order to achieve contiguous pathways for electrons and holes. Comparing the chemical structure of several polymers (including the polymers mentioned above) with the dependence of the solar cell efficiency with blending ratio, suggests that this intercalation is a common problem and needs to be addressed in the future design of polymers.

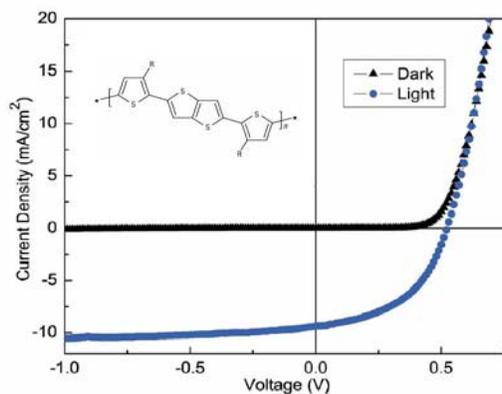


Figure 8: IV curve for a 1:4 pBTTT:PC_[71]BM in the dark and under AM 1.5 solar irradiance showing an efficiency of 2.35%. The inset shows the pBTTT monomer.

In order to check for intercalation, the phase separation must be studied using a variety of techniques. Large-scale phase separation is not the problem, as one would expect from the fact that pBTTT forms ‘giant’ crystals, because the photoluminescence is quenched for all ratios and annealing. This leaves the possibility that at lower PCBM-loading, there is inadequate phase separation. In order to answer this question McGehee has developed x-ray techniques to explore pBTTT:PCBM films with a varying amount of PCBM. Measurements of the lamellar stacking perpendicular to the substrate (figure 9a) show that as more PCBM is added, a new peak emerges that corresponds to a d-spacing that is 1 nm larger. This expanded d-spacing could be due to intercalation of the PCBM molecules into the molecular stack as the difference in d-spacings is roughly the size of a PCBM molecule. A possible schematic of what this would look like in both face-on and as a space-filling side-view is shown in figure 9b.

Unpublished results cannot be posted at this time due to requirements of the journal we plan to publish these research in

Figure 9: a) Specular x-ray scattering of pBTTT:PCBM blends showing an expansion of the d-spacing with increased PCBM. b) Schematic of how the PCBM intercalates into the pBTTT crystals

The veracity of this picture was confirmed using grazing-incidence x-ray scattering with an area detector (figure 10a) and small angle scattering (figure 10b). The latter technique has never been used for the analysis of polymer solar cells, but is used to determine internal phase separation on the nanometer scale in a variety of other systems. Both an increased presence of PCBM (figure 10a) and an increased phase separation (figure 10b) accompany an increase in PCBM-loading. These techniques will be instrumental in the advanced screening of the polymers synthesized by Bao. Once the universality of this result is verified for these polymers, side-chain design will be needed in order to reduce the amount of PCBM needed to optimize the device as the PCBM is a poor absorber of sunlight with a large bandgap.

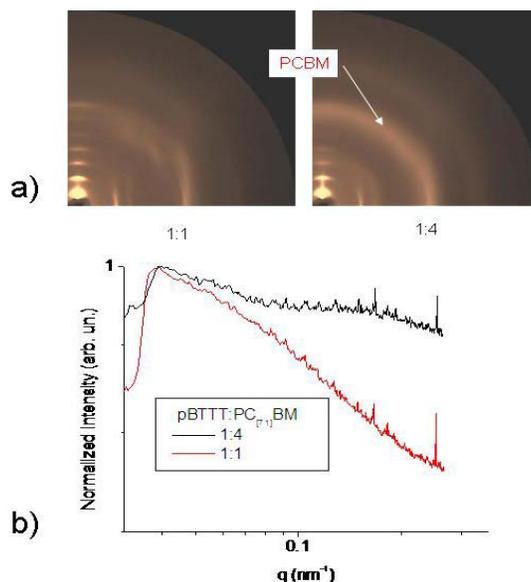


Figure 10: X-ray scattering of 1:1 and 1:4 pBTTT:PCBM blends showing increased phase separation with increased PCBM Concentrations a) 2D grazing-incidence x-ray scattering and b) small angle x-ray scattering.

Publications:

- 1) M. Tang, A. Reichardt, N. Miyaki, R.M. Stoltenberg, Z. Bao, **J. Am. Chem. Soc.** accepted.
- 2) M. Tang, A. Reichardt, Z. Bao, **Adv. Func. Mater.**, in press.
- 3) M. Tang, A. Reichardt, T. Siegrist, S.C.B. Mannsfeld, Z. Bao, **Chem. Mater.** in press.
- 4) T. Okamoto, Y. Jiang, F. Qiu, A.C. Mayer, J.E. Parmer, M.D. McGehee, Z. Bao, **Macromolecules**, accepted.
- 5) T. Okamoto, M.L. Senatore, M.M. Ling, A.B. Mallik, M.L. Tang, Z. Bao, **Adv. Mater.** 19, 3381-3384, 2007.
- 6) T. Okamoto, Z. Bao, **J. Am. Chem. Soc.** 129, 10308-0309, 2007.
- 7) S. Sista, Y. Yao, Y. Yang, M.L. Tang, Z. Bao, **Appl. Phys. Lett.** 91, 223508, 2007.
- 8) J.E. Parmer, A.C. Mayer, B.E. Hardin, S.R. Scully, M.D. McGehee, M. Heeney, I. McCulloch, **Applied Physics Letters** 92 (2008) p. 113309-1-3.
- 9) A.C. Mayer, S.R. Scully, B.E. Hardin, M.W. Rowell, M.D. McGehee, **Materials Today**, 10 (2007) p. 28-33.
- 10) S.R. Scully, P. B. Armstrong, C. Edder, J.M.J. Frechet, and M.D. McGehee, **Advanced Materials** 19 (2007) p. 2961-6.

References:

1. Jundt, C., et al., *Exciton Dynamics in Pentacene Thin Films Studied by Pump-Probe Spectroscopy*. Chem. Phys. Lett, 1995. **241**: p. 84-88.
2. Paci, I., et al., *Singlet Fission for Dye-Sensitized Solar Cells: Can a Suitable Sensitizer Be Found?* J. Am. Chem. Soc., 2006. **128**(51): p. 16546-16553.
3. Yoo, S., B. Domercq, and B. Kippelen, *Efficient thin-film organic solar cells based on pentacene/C60 heterojunctions*. Applied Physics Letters, 2004. **85**(22): p. 5427-5429.
4. Lupton, J.M. and J. Klein, *Hot band emission and energy transfer in organic electrophosphorescent devices*. Chemical Physics Letters, 2002. **363**: p. 204-210.
5. Baldo, M.A., et al., *Excitonic singlet-triplet ratio in a semiconducting organic thin film*. Physical Review B, 1999. **60**(20): p. 14422.
6. Okamoto, T. and Z.A. Bao, *Synthesis of solution-soluble pentacene-containing conjugated copolymers*. Journal of the American Chemical Society, 2007. **129**(34): p. 10308-+.
7. Okamoto, T., et al., *Synthesis and Characterization of Pentacene- and Anthradithiophene-Fluorene Conjugated Copolymers Synthesized by Suzuki Reactions*. Macromolecules, 2008: p. in press.
8. McCullough, R.D., et al., *Design, synthesis, and control of conducting polymer architectures: structurally homogeneous poly(3-alkylthiophenes)*. J. Org. Chem., 1993. **58**: p. 904-912.
9. Roncali, J., *Synthetic principles for bandgap control in linear pi-conjugated systems*. Chemical Reviews, 1997. **97**(1): p. 173-205.
10. Pan, H.L., et al., *Low-temperature, solution-processed, high-mobility polymer semiconductors for thin-film transistors*. Journal of the American Chemical Society, 2007. **129**(14): p. 4112-+.

11. O'Regan, B. and M. Gratzel, *A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO₂ Films*. Nature, 1991. **353**: p. 737-40.
12. Bach, U., et al., *Solid-state dye-sensitized mesoporous TiO₂ solar cells with high photon-to-electron conversion efficiencies*. Nature (London), 1998. **395**(6702): p. 583-585.
13. Kuang, D., et al., *Organic Dye-Sensitized Ionic Liquid Based Solar Cells: Remarkable Enhancement in Performance through Molecular Design of Indoline Sensitizers*. Angew. Chem. Int. Ed., 2008. **47**: p. 1-6.
14. Schmidt-Mende, L., S.M. Zakeeruddin, and M. Gratzel, *Efficiency improvement in solid-state-dye-sensitized photovoltaics with an amphiphilic ruthenium-dye*. Applied Physics Letters, 2005. **86**(1): p. 13504-1.
15. Liu, Y.X., Summers, M. A., Scully, S. R., McGehee, M. D., *Resonance Energy Transfer from Organic Chromophores to Fullerene Molecules*. Journal of Applied Physics, 2006. **99**: p. 093521.

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